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AUTOPSY AND CHARACTERIZATION OF NF MEMBRANES AFTER LONG-TERM OPERATION IN A NF-SWRO PILOT PLANT*

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ABSTRACT

With the new approach to seawater desalination processes, which was developed at Saline Water Conversion Corporation (SWCC), R&D Center, the nanofiltration (NF) membrane pretreatment process is used to supply feed/make-up to operate conventional seawater desalination plants. The seawater treatment first with the NF membrane removed from it turbidity and microorganism, caused significant rejection of the scale forming hardness ions, reduced TDS in Gulf Seawater and produced a new, partially desalinated seawater product, considerably different and superior to seawater in qualities and without the problems normally associated with seawater. The said desalination arrangements lead to a significant improvement in the seawater desalination processes. The NF pilot plant used in above investigation has been in continuous operation for over 10,000 hours. The pretreatment of the nonchlorinated seawater feed (taken from an open intake) to the NF pilot plant was limited to simple, nonchemical dual media filtration without coagulation. The differential pressure across the NF membrane remained steady at about 15 psi (≈1 bar) during the entire pilot plant operation. After the 10,000 hours of continuous NF pilot plant operation, an autopsy analyses of two membranes among the 10 membranes were performed, which includes, biological, chemical and physical analyses of membranes and foulant deposits on its surfaces. It was found that the lead element surface was covered with thick reddish brown slimy deposits whereas the last element was relatively clean, with slight deposits only. The deposits constitutes mainly the primary organic matter, iron, chromium, in addition to the chemical constituents usually found in the seawater. Also, scale forming

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hardness ions in significant quantity were absent in the foulant deposits in spite of not using any acid or antiscalant during the most of the operation period. Permeate recovery was less than 50%. The presence of iron is mainly from corrosion of the stainless steel piping as well as from the ferric deposits which were trapped in the media filter and escaped later during the pretreatment. Even though few diatoms could be seen on the membrane surfaces, bacteriological analyses and the amount of primary organic matter indicates that the membranes are not biofouled despite no biocide was used during the long term operation of NF unit.

1. INTRODUCTION

For the first time ever, a new approach to seawater desalination processes by integrating the nanofiltration (NF) membrane process with one of the conventional desalination processes to form, for example, an NF-SWRO or NF-MSF or a combination thereof, such as NF-SWRO$_{reject}$-MSF, was developed at Saline Water Conversion Corporation (SWCC), R&D Center, and was successfully applied to those cases on a pilot plant scale with remarkable results. The seawater treatment first with the NF membrane removed from it turbidity and microorganism, caused significant rejection of the scale forming hardness ions, produced a new seawater product, considerably different and superior to seawater in qualities. The said desalination arrangements lead to a significant improvement in the seawater desalination processes by lowering their energy consumption, and chemical consumption thereby making the process more friendly to the marine environment, as well as by doubling their product water output and recovery ratio with the ultimate benefit of lowering the cost of fresh water production [1-4].

During this breakthrough experiment, NF pilot plant consisting of 10 NF membranes of size 4″ × 40″ were operated at different pressures for more than one year to supply feed water to SWRO as well as the MSF pilot plants. Like most of the membrane processes, NF membrane can also suffer from fouling which could lead to reduction in its performance. It was also reported in many instances, where NF membrane have been used for treating the surface water, that the performance remarkably declined, during short period of operation [5-7]. In the present study, after about 10,000 hrs. of operation

the product flux of the NF membranes declined and, it was decided to remove some of the membranes and autopsy them so as to find out the reason for the decline in their performance. The entire work, however, was made with one type of membrane which is identified in reference [8] as NF-A membrane.

2. EXPERIMENTAL

A schematic flow diagram of the NF pilot plant is shown in Figure 1. The NF pilot plant consists of seawater supply system, dual media filter followed by fine sand filter, 5 μ cartridge filter, feed tank and the NF unit. The NF unit consists of the high pressure pump and five NF modules (V5 - V9) each containing two commercial NF membrane elements (size 4"x40"). The feed is supplied to the first two modules, arranged in parallel, and the reject of each is fed to its following module, which is connected to it in series. Reject from the latter two modules constitutes the feed for the final fifth module. After its filtration without coagulation, the filtrate was passed to the NF membrane under pressure, initially of about 18 bar. This was followed by passing the product from the NF unit to the SWRO unit, or alternatively NF permeate or SWRO reject from an NF-SWRO pilot plant, was fed to the MSF unit as shown in Figure 1.

The NF unit was operated continuously without adding acid except occasionally and for short time to reduce the feed pH to 7.0. During the winter months, to offset the effect of decline in NF feed temperature on NF product flow the NF feed pressure was raised to reach 31 bars. During the whole NF-SWRO and NF-MSF experiments no chemicals were added as coagulant or as scale control acid treatment. Chlorine when present in the feed was removed prior to the NF unit by dosing sodium bisulfite. Chemical, biological analyses, and membrane system performance parameters were measured for the seawater, the permeate and reject at the various stages of the process on a routine basis.

At the end of 10,000 h operation two elements, viz., the feed side element from the module V6, (henceforth known as lead element) which is one of the lead element as well as the brine side element (henceforth known as last element) from the vessel V9 which is the last element in the membrane series were removed for autopsy purpose.

Before removing the membranes from their respective module each modules performance were determined.

Autopsy and analyses were conducted on all membranes using the standard procedure adopted for SWRO membranes in the earlier studies [9]. It involved cutting open the membrane, visual inspection of surface, estimation of amount of deposits on the membrane surface after drying, chemical analyses of deposits using Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP) and bacterial enumeration on membrane surface. After removing the samples for bacterial enumeration, foulant deposits were scrapped off from the surface and thoroughly dried before analyzing for various inorganic elements using AAS and ICP. Also, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses were conducted on representative samples cut from the membranes which were thoroughly dried and were used without any cleaning.

For bacterial enumeration, membranes were aseptically dissected and excised pieces of membranes from feed and brine sides were removed each into a sterile petri dish containing 9 ml of sterile saline. The bacteria on membrane surfaces were scrapped out and the area of each piece of membrane were determined. The bacterial suspension was then pipetted into sterile test tubes and dispersed by vortex mixing. The suspension in each test tube was serially diluted in 10 fold steps and 1 ml from suitable dilutions was mixed with molten marine agar at 46^{o}C using pour plate technique. The plates were incubated in a constant temperature incubator for 96 h. The number of bacteria was obtained as colony forming units (CFU) and expressed as CFU/cm^2.

3. RESULTS AND DISCUSSION

At the end of the 10,000 h operation of NF membranes in the aforementioned arrangement, the total normalized product flow of NF membranes were decreased from a value of about 16 l/min to about 11.2 ml/min amounting to a 30% decline. Before performing autopsy, the performance of each of the five modules (contains two NF elements) were determined and the obtained normalized product flow are tabulated in Table 1. It can be observed that the modules containing lead elements (V5 & V6) are

having the least performance. The performance of remaining elements was better as we progressively move to the last element as can be seen from the same table. Only one of the lead element was autopsied along with last element for comparison.

The visual inspection of the lead element which had lowest product flow was found to be completely covered with reddish brown colored slimy deposits throughout the membrane leaves (see Figure 2) which can be easily scrapped and dry weight of these deposits amount to about 1.55 mg/cm^2 of membrane area. Whereas, the last element which had the highest permeate flux, was relatively clean and only a thin reddish brown coating of the same kind of deposits found on the lead element were observed on its surface (see Figure 3) and dry weight of this thin deposit is only about 0.33 mg/cm^2 of the membrane area as can be seen from the Table 2. This indicates that most of the foulant deposits are accumulated on the surface of the lead element, and these deposits are mainly responsible for about 35% of flux decline of the lead element compared to the last elements.

The detailed chemical analyses of the foulant deposits scrapped off from the surface of the membranes reveal that other than the primary organic matter, the iron (Fe) constitute the major inorganic chemical component in these deposits for both lead and last element. Fe forms about 25% and 12.5% in lead and last element, respectively and must have deposited on the membrane surface as a result of corrosion of the stainless steel piping. This assumption is supported by the presence of about 5.1% and 2.8% of Cr respectively in the lead and last element respectively. However, presence of large amount Fe prompted us to examine other source of iron deposition. Since, during the entire experiment, coagulant based on iron (such as $FeCl_3$) or other chemicals were not used, possibility of iron from these sources can be ruled out. Nevertheless, the present NF unit was using the same pretreatment unit which was used for evaluating SWRO membrane in earlier studies [9], where $FeCl_3$ was used as coagulant and also the kind reddish brown deposits found on membranes were also found on those SWRO membranes. This made us to open up and inspect the media filters to find out any residual Fe trapped between the media. It was observed that lumps of Fe deposits were trapped in between the media. These trapped Fe could have possibly escaped slowly during the long-term non-coagulant dosing operation of NF unit and got deposited on

the membrane surface. It is also observed that the amount of both Fe and Cr reduced to 50% in the last element compared to the lead element (see Table 2).

Rest of the chemical constituents in the foulant deposits are very little in quantity except the chloride and sulfur, both of which could be expected because of the seawater feed itself. It is interesting to note that scale forming hardness ions such as calcium and magnesium are not found in significant quantities in these foulant deposits, despite NF unit was in operation most of the time without dosing any antiscalant chemicals or acid. This was also true for the last element, which is exposed to highly concentrated feed containing high concentration of hardness ions. The absence of scale forming ions may be related to the relatively low permeate recovery of less than 50%.

The loss on ignition, which is the indication of the primary organic matter were about 46.5% and 61.2% for both the lead and last elements respectively. These values suggest that the membranes possibly may not have biofouled, if so the value could have been more than 70% as reported by Flemming [10] and more than 50% as reported by Baker and Dudley [11]. Moreover, the bacteriological analyses supports the absence of biofouling on these NF membranes as can be seen from the bacteria count analyses which are given in Table 3. Here, the colony forming unit (CFU) count for both the membranes at their respective feed and brine side end of the element were well below the value of 10_5 CFU/cm^2 according to Flemming [10] as well as 10^6 CFU/cm^2 according to Baker and Dudley [11] which are lower limit values of biofouled membranes. Hence, it can be clearly stated that even though no chlorination or disinfection methods were used during the long term NF operation, the membranes were not biofouled.

However, the SEM and EDX studies of this membrane reveal some interesting results. The study indicates presence of very few diatoms on the membrane surface as can be seen from Figure 4. EDX spectrum of the same show predominant Si peak, which confirms it to be a diatom. However, these diatoms cannot survive and thrive on membrane surface on account that they are autotrophic in nature and they cannot get required sunlight, which is essential for its food preparation by photosynthesis.

The SEM and EDX results obtained from both membranes are shown in Figures 5 & 6 Lead element (Figure 5) show that its surface is thickly covered with deposits, whereas last element (Figure 6) surface is relatively clean. Moreover, EDX spectra of both elements show that, the elemental compositions are similar for both the membranes and it supports the chemical analyses results of the deposits. Here, predominant peaks are of O, Fe, Cl, Na, S, Cr etc., most of which were also found during the chemical analysis of the foulant deposits. The major peak of course is due to Fe, which forms the major inorganic foulant as was confirmed by the chemical analyses results. Other chemical constituents are of minor in nature. The peaks due to sulfur could be both from the sulfate deposited on the membrane surface as well as the from the polysulfone support of the TFC membrane.

4. CONCLUSION

In conclusion it can be said that the foulant deposits found on the membrane surface may have partially contributed in reducing NF membrane performance, especially the lead element membrane. The foulant mainly consists of primary organic matter and Fe, which escaped from the media filter after being trapped between the media and also as a result of corrosion of stainless steel piping as supported by presence of Cr. No membrane scaling occurred in spite of no antiscalant or acid were used during most of the operation. Operation of NF unit without disinfection did not cause any biofouling for the NF membranes.

5. ACKNOWLEDGMENTS

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Table 1. Individual module (2 elements/vessel) performance at the end of NF operation

Vessel number	Normalized Flow (liter/minute)
V5	1.8
V7	2.0
V6	1.8
V8	2.9
V9	2.7

Table 2. Foulant deposit analyses results on NF membranes

Parameter	**Membrane**	
(%)	**Lead Element**	**Last Element**
Ca	0.41	0.42
Fe	24	12.5
Cr	5.1	2.8
Cu	0.05	0.03
Mg	0.24	0.49
Ni	0.01	ND
Si	0.08	0.09
Cl	2.9	7.2
S	5.5	3.4
Loss on ignition at 550 ^{o}C	46.5	61.2
Foulant per unit area (mg/cm^2)	1.55	0.30

ND = Not detected

Table 3. Bacteria count on the membrane surface

	No. of Bacteria (CFU/cm^2)	
Membrane	Lead Element	Last Element
Feed Side	1.34×10^4	5.88×10^3
Brine Side	2.45×10^4	7.32×10^3

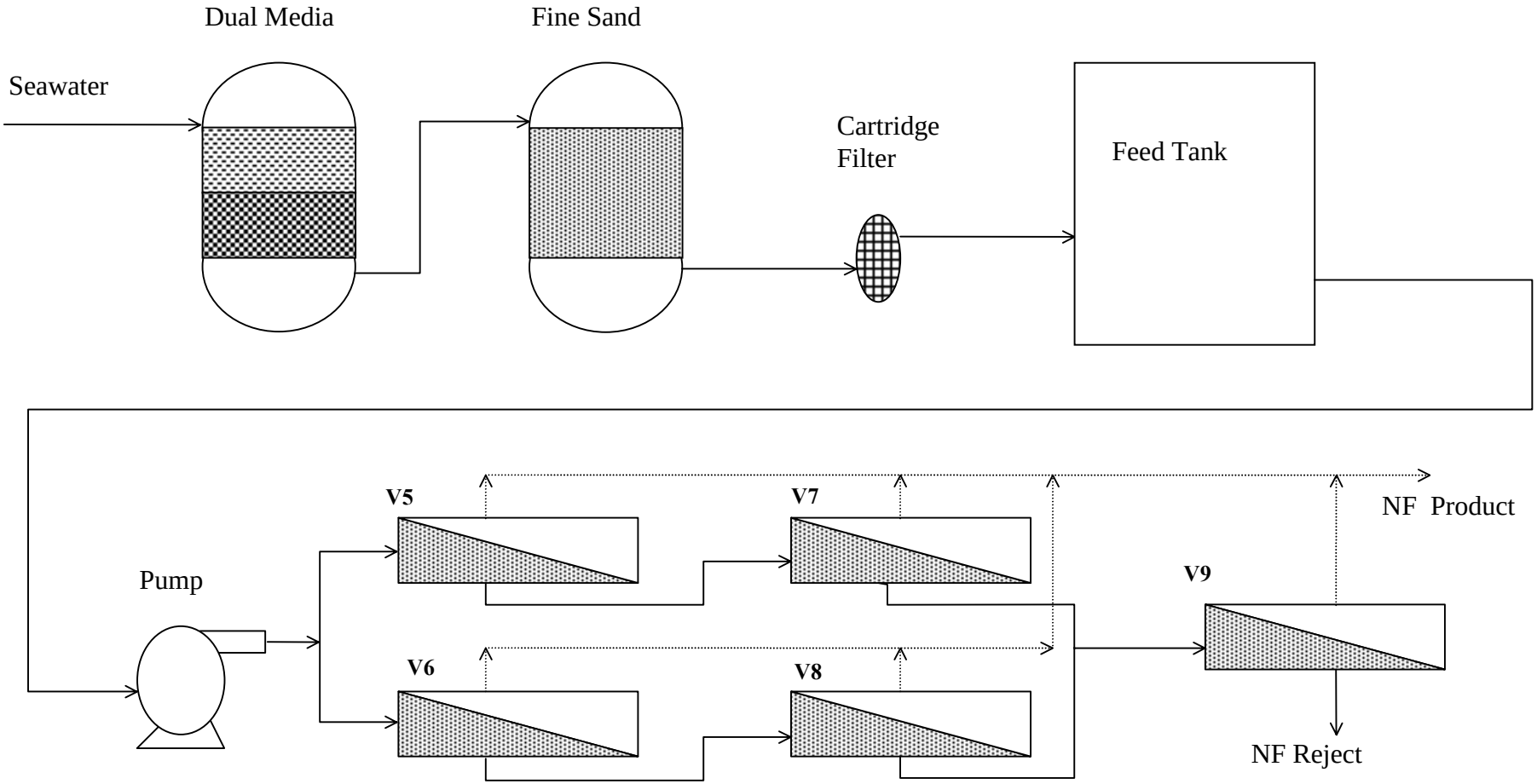


Figure 1. A Schematic Flow Diagram of Seawater Pretreatment Pilot Plant Using NF Membranes showing the Arrangement of NF Membranes

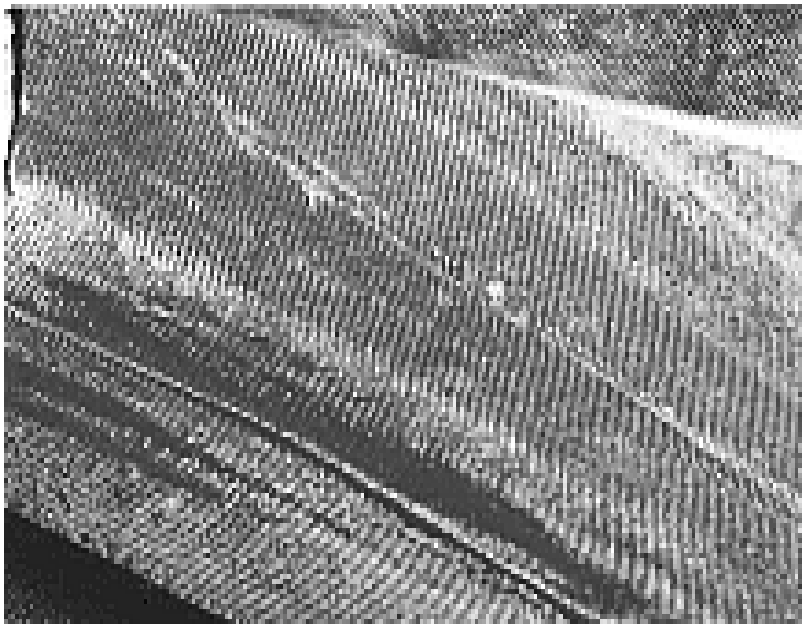


Figure 2. Photograph of lead element NF membrane surface

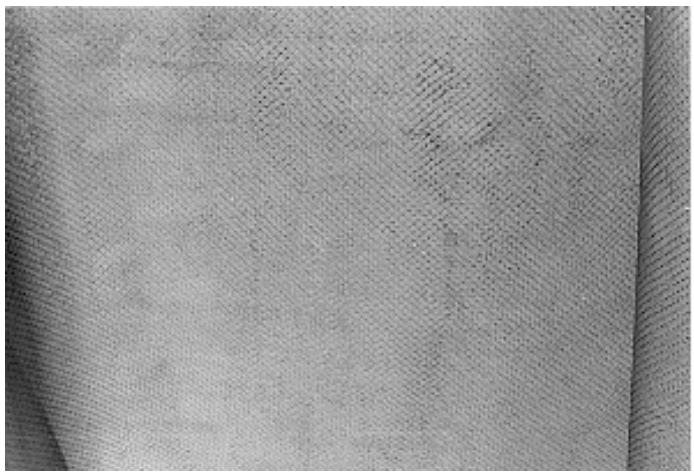


Figure 3. Photograph of last element NF membrane surface

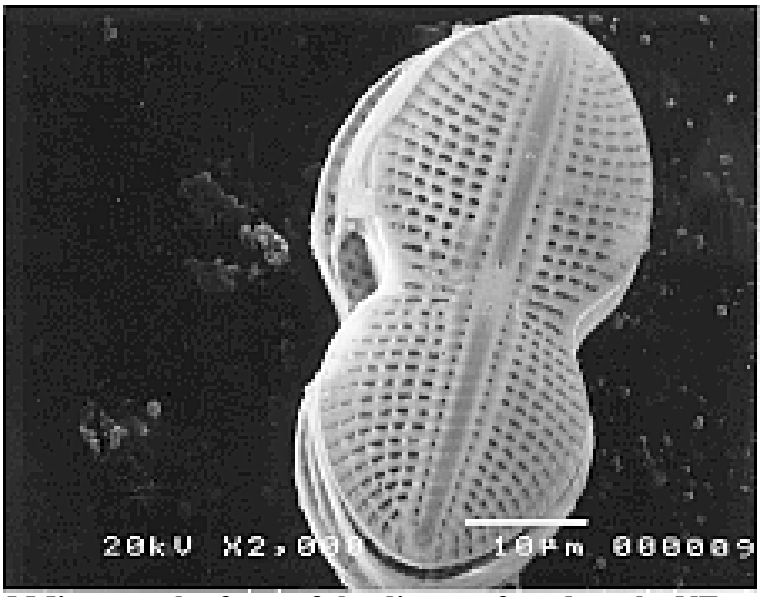
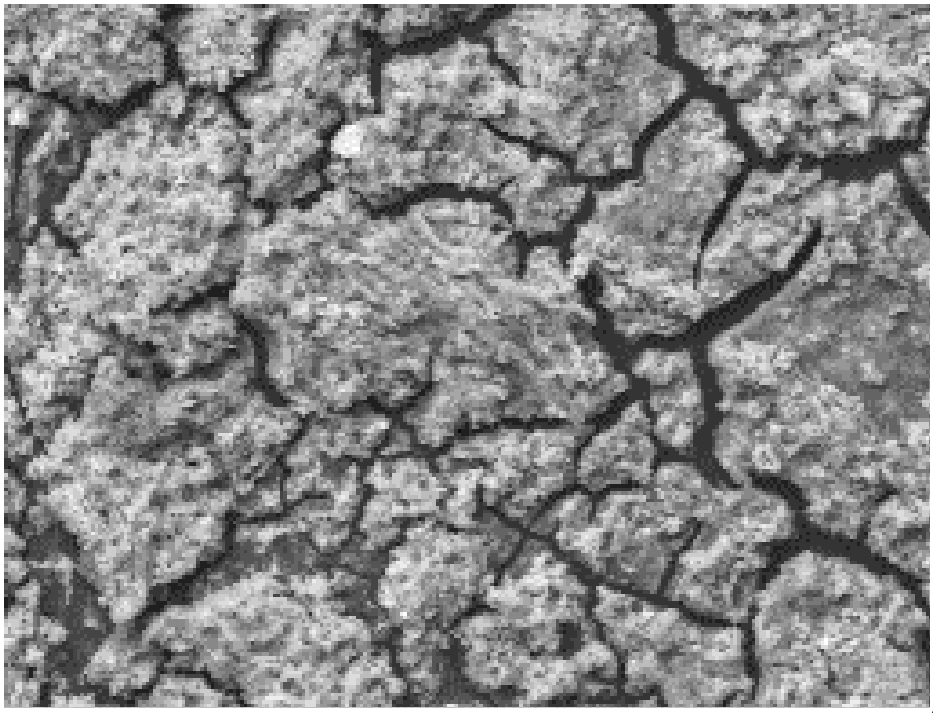


Figure 4. SEM Micrograph of one of the diatoms found on the NF membrane surface



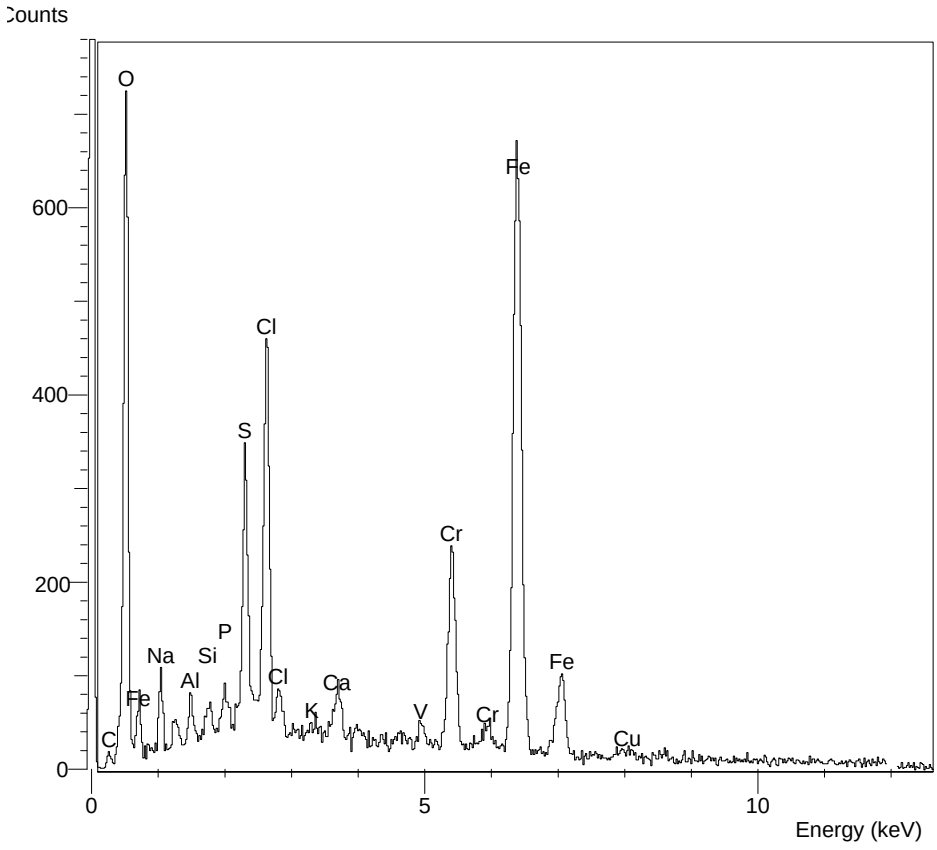
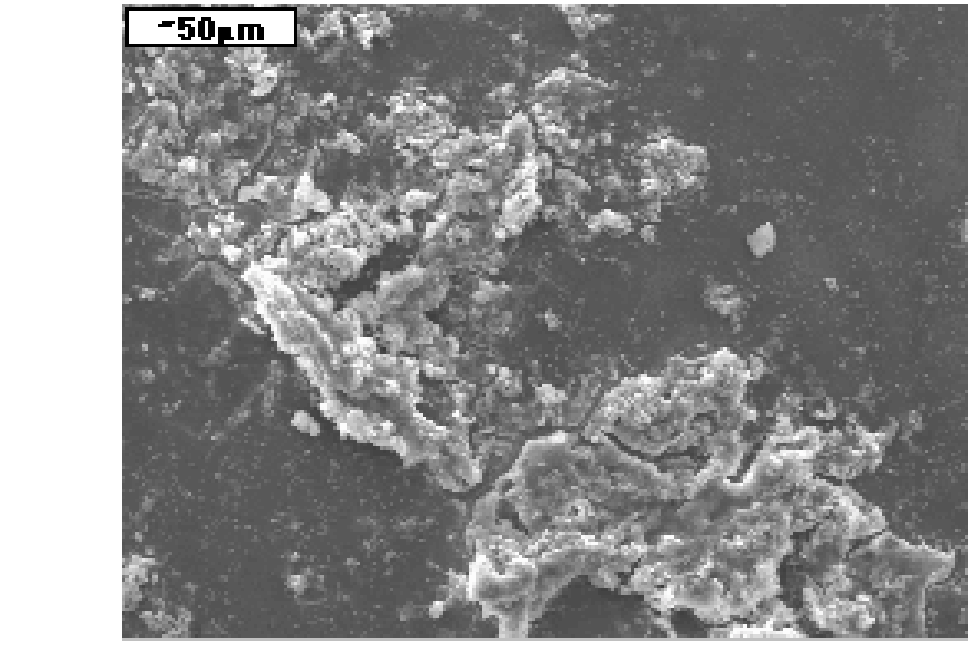


Figure 5. SEM micrograph and EDX spectra of lead element



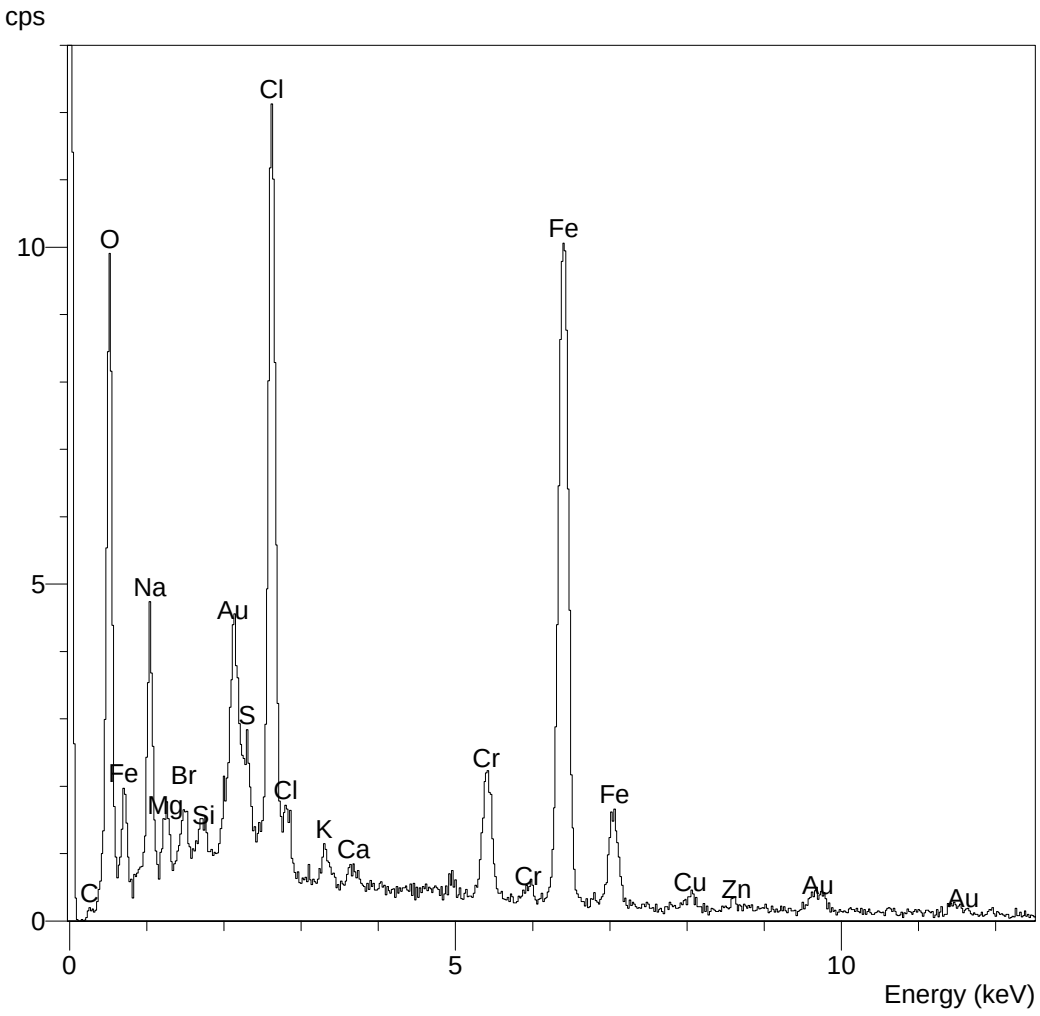


Figure 6. SEM micrograph and EDX spectra of lost element

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